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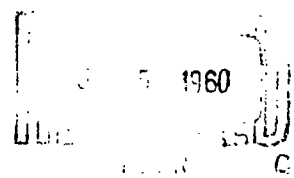
**MODIFICATIONS IN THE NRL COLORIMETRIC METHOD
FOR THE DETERMINATION OF
BIS(2-CHLOROETHYL)SULFIDE WITH DB-3**

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Chemistry Division

May 16, 1960

XEROX



**U. S. NAVAL RESEARCH LABORATORY
Washington, D.C.**

ABSTRACT

A program was undertaken to study and improve the present NRL colorimetric method for the determination of bis(2-chloroethyl)sulfide, commonly known as mustard gas. That part of this program which has been directed toward improving sensitivity and color stability has established the fact that hexylene glycol and Methyl Cellosolve are more effective solvents than diethyl phthalate, especially when determining residual quantities of mustard in paint films.

Inorganic alkalies such as aqueous solutions of sodium carbonate, potassium carbonate, and sodium hydroxide were found to be more stable than cyclohexylamine as developing agents.

The effects of pH, age, water content, and heating time on the DB-3 solutions were determined and it was found that the only modification which improved the sensitivity was in the heating period of the mustard-containing DB-3 solution, and accordingly the heating period was changed from 5 to 4 minutes.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C08-22
Project NS 097-001

Manuscript submitted October 19, 1959.

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INTRODUCTION

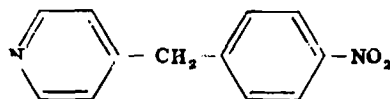
Background

Bis(2-chloroethyl)sulfide, commonly called mustard gas and designated H, is a toxic agent which is likely to be sorbed in such substances as paint films, charcoal, and textiles. Colorimetric techniques for H determination have been previously devised utilizing 4-(p-nitrobenzyl)pyridine (DB-3) as the color reagent. Although there are several quantitative analytical methods for H determination, the colorimetric analysis is best suited for estimating small amounts of residual H.

Chichibabin (1) in 1925 reported the preparation of DB-3 and its methiodide color reaction on treatment with alkali, and in 1941 Brown (2) reported the use of DB-3 as a color reagent for the detection of H. The analytical procedure for the colorimetric determination of H with DB-3 was developed by Swift, Nieman, and Holzman (3) and was refined at this Laboratory by Taylor, Stokes, and Carhart (4).

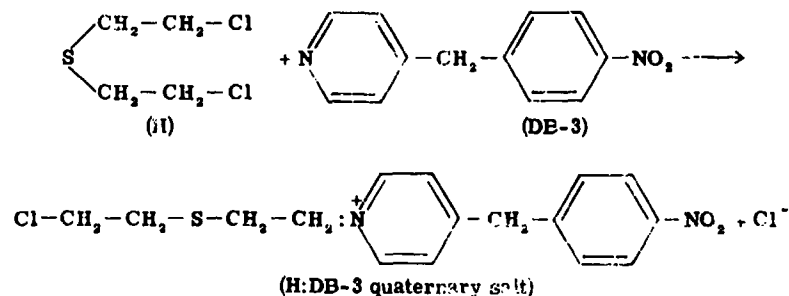
The Role of DB-3

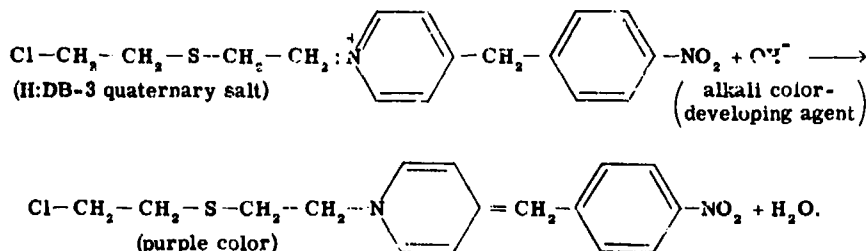
DB-3 has the following structure:



It will react with any compound containing an alkylating functional group to give a pyridinium compound which in turn can be converted to a highly colored basic form by the addition of alkali. This reaction takes place in two steps:

Coupling



RearrangementThe Nature of the Problem

Preliminary investigations have shown that the methods of Swift, Nieman, and Holzman (3), and of Taylor, Stokes, and Carhart (4) are not entirely satisfactory for quantitative determination of H that has been sorbed into paint films, particularly those used on naval ships and installations. Sensitivity and color stability were found to be less than desired and it was believed that an extractor solvent other than diethyl phthalate might correct the deficiencies. At the same time a search was started for a more stable alkali color-developing agent. Therefore, analytical modifications in the Taylor, Stokes, and Carhart method were sought in three major aspects: (a) sensitivity, i.e., colorimetric units per microgram of H, (b) color stability, and (c) adaptability to analysis of H in paint films, i.e., negligible hydrolysis and/or oxidation of H in the solvent chosen.

MATERIALS UNDER CONSIDERATION

The present study explores the use of diethyl phthalate, hexylene glycol (5), and Methyl Cellosolve as solvents. Diethyl phthalate is the solvent used by previous investigators (3,4). Some objections to the use of diethyl phthalate are its immiscibility with water and consequent difficulty in cleaning glassware, and its difficulty of extracting H from paint films. Hexylene glycol and Methyl Cellosolve are relatively free from these disadvantages, and, in addition, their use introduces increased analytical sensitivity and stability.

The color-developing agents investigated were cyclohexylamine (1:1 by volume of cyclohexylamine and Methyl Cellosolve), piperidine, 0.25 N NaOH, 0.25 N K₂CO₃, 0.25 N Na₂CO₃, 0.50 N Na₂CO₃, 1.0 N Na₂CO₃, and 2.0 N Na₂CO₃. The disadvantages of using cyclohexylamine are that it absorbs carbon dioxide from the atmosphere, consequently forming a white solid, and that it darkens on standing. These disadvantages make it highly desirable that other developing agents be found. Piperidine was included in the investigation because it has been used as a developing agent (3) and also to make a comparison with the inorganic* color-developing agents used.

*Swift, Nieman, and Holzman suggested sodium carbonate as a developing agent, but it was found incompatible with their procedure.

PROCEDURE AND RESULTS

The analytical procedure followed was the NRL method (4); twice recrystallized DB-3 (6) was used unless otherwise stated. In all cases, the analytical results were obtained with a Klett-Summerson (K-S)* colorimeter using a #54 green filter.

Solvents and Developing Agents

Using the NRL method, various solvents and developing agents were examined for the presence of oxidizing agents, for sensitivity, and for color stability. Tests of the three solvents indicated an absence of oxidizing agents. The results for the developing agents are given in Table 1. The table indicates that, in addition to cyclohexylamine, 0.25 N Na_2CO_3 is a satisfactory developing agent. Also, according to the table in its entirety, the results show that both hexylene glycol and Methyl Cellosolve compare favorably with diethyl phthalate as an H solvent. This evidence is corroborated by the curves in Figs. 1 and 2.

Using Methyl Cellosolve as the H solvent, all the developing agents under consideration were used. One-ml samples of the organic developing agents were tested by using them as prescribed in the NRL method. Preliminary investigation revealed that samples from 1 to 5 drops of the inorganic developing agents were suitable for use, and therefore one drop of agent was chosen as an arbitrary standard. The results (Figs. 3a, 3b, and 3c) show that the inorganic developing agents compare favorably with cyclohexylamine, and moreover they are stable in that, unlike cyclohexylamine, they do not absorb carbon dioxide from the atmosphere nor darken on standing.

Table 1
Effect of Different Solvents and Developing Agents
on Sensitivity and Color Stability in
H-Containing DB-3 Solutions

Solvent and Developing Agent	Sensitivity (Net K-S Reading) (γ H)	Color Stability* (minutes)
Diethyl phthalate		
Cyclohexylamine	3.9	60
0.25 N Na_2CO_3	6.1	41
Hexylene glycol		
Cyclohexylamine	5.8	42
0.25 N Na_2CO_3	6.0	240
Methyl Cellosolve		
Cyclohexylamine	6.1	36
0.25 N Na_2CO_3	6.4	30

*The length of time for color to disappear.

*All recorded K-S readings are net readings obtained by subtracting the reading of a blank from the reading of an H-containing sample.

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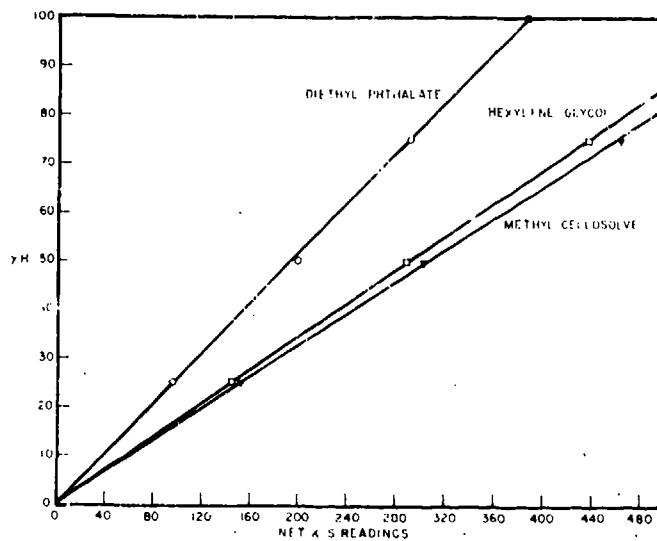


Fig. 1 - Effect of various solvents and cyclohexylamine in H-containing DB-3 solutions

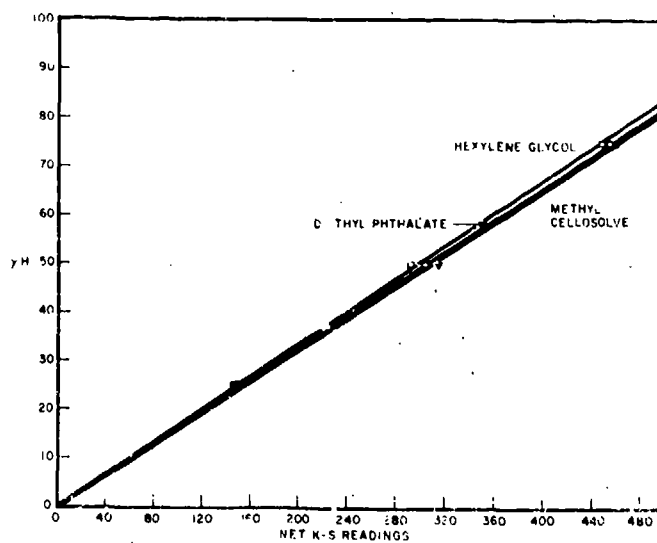
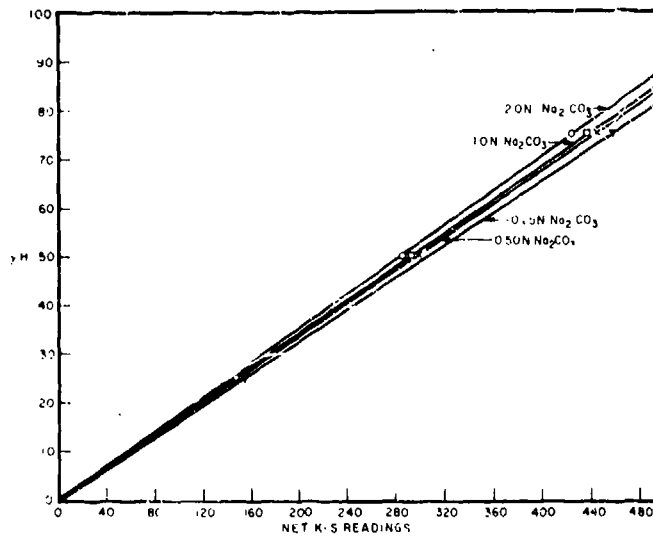
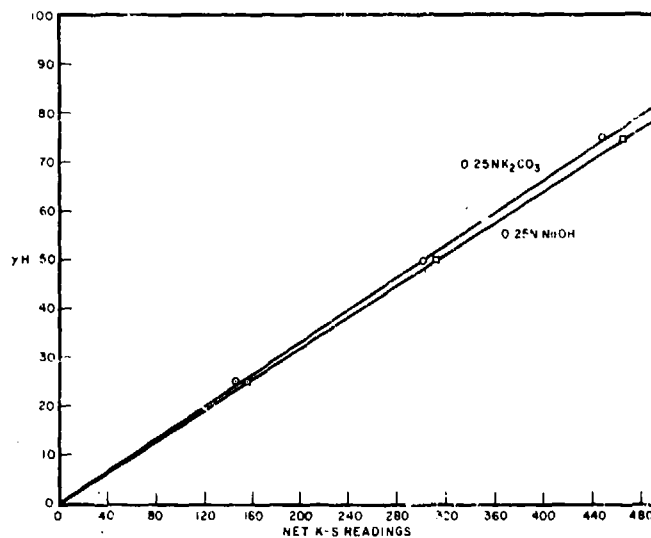


Fig. 2 - Effect of various solvents and 0.25 N Na_2CO_3 in H-containing DB-3 solutions

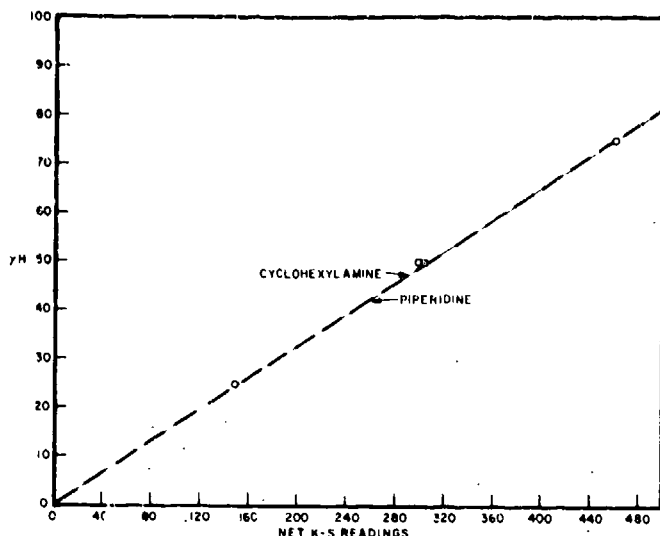


3a - 0.25, 0.50, 1.0, and 2.0 N Na_2CO_3



3b - 0.25 N K_2CO_3 and 0.25 N NaOH

Fig. 3 - Effect of various developing agents and Methyl Cellosolve in H-containing DB-3 solutions



3c - Cyclohexylamine and piperidine

Fig. 3 (continued) - Effect of various developing agents and Methyl Cellosolve in H-containing DB-3 solutions

DB-3 Solutions

Variation with Age - Samples of DB-3 from 2 sources were used to prepare the solutions. One was a 14-year-old laboratory shelf sample, and the other, twice recrystallized by the author, was obtained from the Defence Research Chemical Laboratory, Canada. Results (Fig. 4) of experiments with samples of DB-3 of varying age indicate that twice-recrystallized DB-3, mp 69.4° to 70.5°C, was more sensitive than the 14-year-old material, mp 65.5° to 57°C, especially in the regions of higher H concentrations.

Variation of pH - The pH of the DB-3 solutions was adjusted by means of dilute perchloric acid. The results (Fig. 5) confirm the evidence of Swift, Nieman, and Holzman (3). It remained for Taylor, Stokes, and Carhart (4) to capitalize on the precision to be gained by pH adjustment. The present study indicates that optimum pH lies between 6.0 and 6.5. The use of pH 6.5 will be retained since no significant difference in sensitivity is obtained with further pH adjustment.

Variation of Water Concentration - The water content of each solution was varied (Fig. 6). The optimum amount of water lies between 10 and 20 ml per 100 ml of DB-3 solution. Since there is no significant difference in sensitivity with 10 or 20 ml of water in making up the solution, the use of 20 ml of water per 100 ml of solution will be retained. Furthermore, the use of 10 ml of water requires longer shaking times for complete solution of the DB-3.

Variation of Heating Time - The heating procedure used for the H-containing DB-3 solutions was that specified for the NRL method, except that the original heating period of 5 minutes was varied (Fig. 7). The 4-minute heating period was significantly different in sensitivity from the others, especially in the region of higher H concentration and for this reason will be included in the modification.

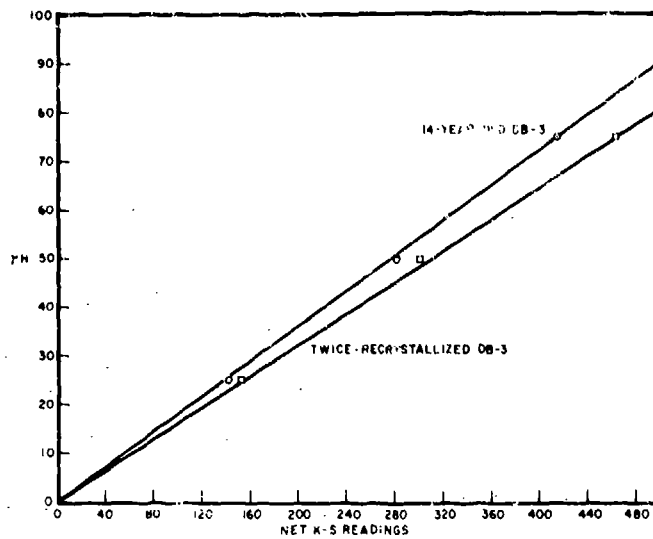


Fig. 4 - Effect of age of DB-3 samples when treated with cyclohexylamine and Methyl Cellosolve

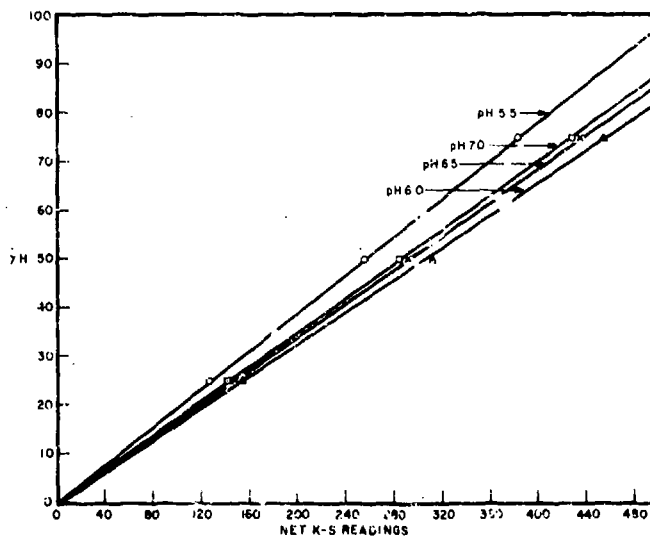


Fig. 5 - Effect of pH of H-containing DB-3 solutions when treated with 0.5 N Na_2CO_3 and Methyl Cellosolve

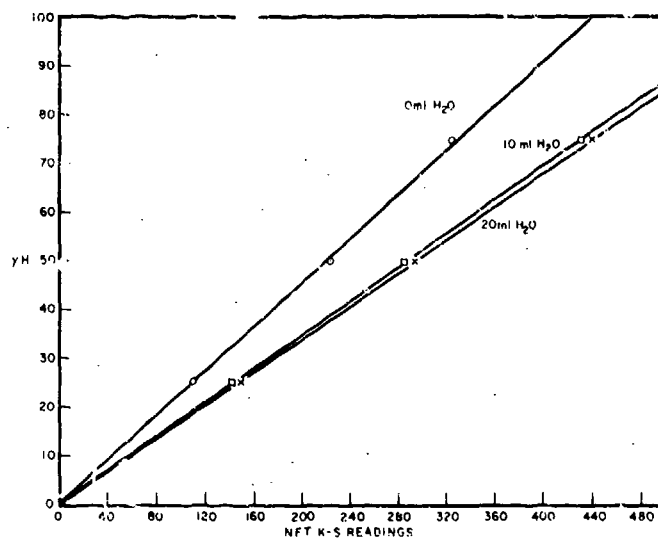


Fig. 6 - Effect of water content of H-containing DB-3 solutions when treated with 0.5 N Na₂CO₃ and Methyl Cellosolve

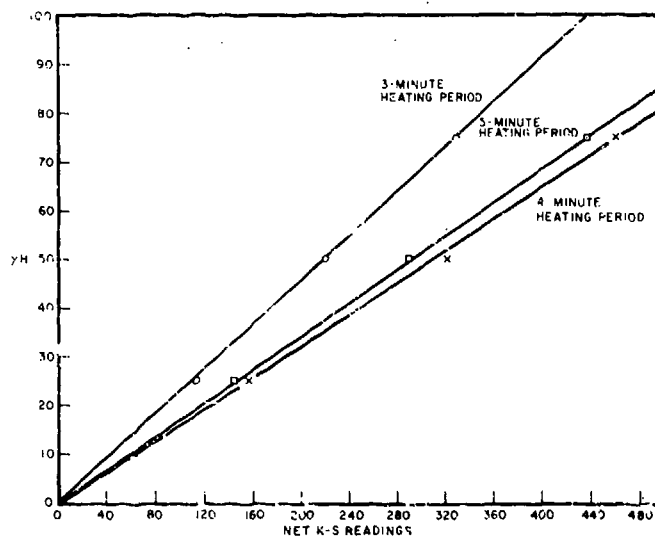


Fig. 7 - Effect of heating period for H-containing DB-3 solutions when treated with 0.5 N Na₂CO₃ and Methyl Cellosolve

MODIFIED METHOD

The preceding experimental results indicated that hexylene glycol and Methyl Cellosolve were quite satisfactory as H solvents. Results also showed that all of the inorganic developing agents as well as piperidine were satisfactory. Although any of the inorganic developing agents could be used in the colorimetric determination of H, the 0.25 N Na_2CO_3 is preferred because it affords greatest sensitivity (Figs. 3a, 3b, and 3c). Too, the sensitivity of the analytical mixture was enhanced by a 4-minute heating period. These aspects have been recommended for incorporation into the regular method and should become part of the modified procedure.

Preparation of Reagents

DB-3 Solution - Three grams of recrystallized DB-3 (satisfactory if the melting point is greater than 69°C), 0.5 gram of sodium perchlorate (NaClO_4), and 20 ml of distilled water are made up to 100 ml with oxidant-free Methyl Cellosolve. The mixture is placed on a wrist-action shaking mechanism until solution is complete. The pH of the solution is adjusted to 6.5 by means of dilute perchloric acid using a pH meter. The adjusted solution is kept in a dark-colored bottle and stored in a refrigerator until needed.

Standard H Solution - A drop of pure H (0.2 to 0.3 g) is weighed into a dark-colored 50-ml volumetric flask (Flask A), which is then filled to the mark with solvent (hexylene glycol or Methyl Cellosolve). From Flask A a sufficient amount of H solution is pipetted into a similar flask (Flask B) so that when this flask is filled to the mark with solvent it will constitute a standard H solution of 25 γH per 1 ml of solution.

Modified Test Procedure

Five milliliters of the DB-3 solution described above should be added to each of 5 K-S colorimeter tubes. Then, in sequence, each tube should receive, individually, a 0, 1, 2, 3, or 4-ml sample of the standard H solution, corresponding to 0, 25, 50, 75, and 100 γH , respectively. Each tube is then filled to the 10-ml mark with solvent (corresponding to that used for the H solution), heated in a water bath (100°C) for 4 minutes, and then cooled in an ice bath (0°C) for 2 minutes. Following this, 1 drop of 0.25 N Na_2CO_3 (0.01 to 0.05 ml) is added to each tube and the solutions should be mixed thoroughly. One minute after addition of the developing agent, the color intensity should be measured through a #54 green filter on the K-S colorimeter. The net K-S reading of the solution being measured is obtained by subtracting from the basic reading of this tube the reading obtained from the first tube, namely the one containing 0 ml of H solution which serves as a blank.

Selecting the H Solvent

The calibration curves of Figs. 8a and 8b show the results of applying the modified method to test samples using hexylene glycol and Methyl Cellosolve as the H solvent. It is evident that, on the basis of sensitivity alone, Methyl Cellosolve and hexylene glycol are interchangeable in this analysis.

Preliminary tests had shown that, with the regular NRL method (4), the quantitative determination of H in paint films was difficult because diethyl phthalate did not extract H

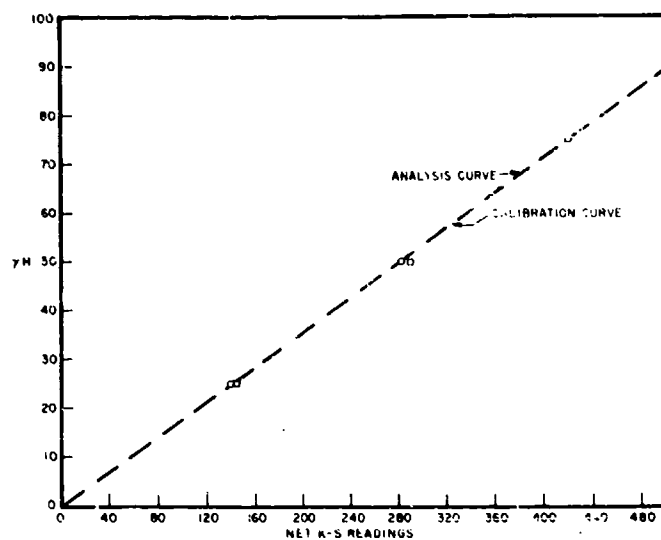


Fig. 8a - Calibration and analysis curves using hexylene glycol as the solvent and determined by the modified method

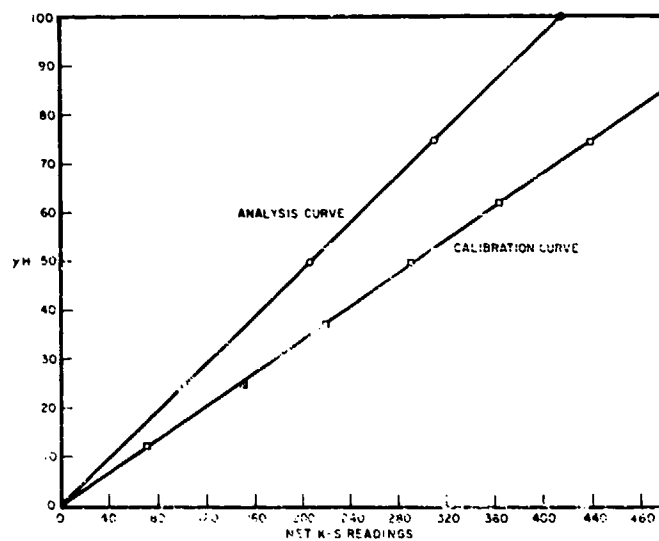


Fig. 8b - Calibration and analysis curves using Methyl Cellosolve as the solvent and determined by the modified method

from paint films readily. To determine the most effective extracting agent, the following test was performed:

One sq-cm metal panels, each with a 0.015-cm-thick coat of dark gray paint containing known amounts of sorbed H, were added to large test tubes each containing 25 ml of solvent (hexylene glycol or Methyl Cellosolve). The tubes were stoppered and placed on the wrist-action shaking mechanism for 20 minutes; preliminary experiments indicated 20 minutes to be sufficient extraction time. The modified procedure was used for quantitative H determination (Figs. 8a and 8b). A study of the calibration and analysis curves indicates that, for determining H quantitatively from paint films, hexylene glycol is the solvent of choice.

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